CO_2-Based Supercritical Fluids as Replacements for Photoresist-Stripping Solvents

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Abstract:

The production of integrated circuits (IC) involves a number of discrete steps which utilize hazardous or regulated solvents. Environmental, safety and health considerations associated with these chemicals have prompted a search for alternative, more environmentally-benign solvent systems. An emerging technology for conventional solvent replacement is the use of supercritical fluids based on carbon dioxide (CO_2).

In this paper, we will first describe the general properties of supercritical fluids, with particular emphasis on their application as alternative solvents. Next, we review the literature results on the possible application of supercritical fluids to several semiconductor processing operations, including the cleaning of silicon wafers, metal deposition, etching, photoresist removal, and waste treatment. Finally, we will describe our recent results on the application of supercritical CO_2 ($SCCO_2$) based fluids to a particular semiconductor processing operation : The stripping of hard-baked photoresists.

Current techniques for hard-baked photoresist removal require the use of highly acidic, highly alkaline or organic solvent systems. We have developed a treatment system, which uses a non-hazardous, non-regulated solvent dissolved in supercritical $SCCO_2$. This system has been sucessfully demonstrated on metallized Si wafers coated with positive-tone photoresists both before and after ion-implantation. Nuclear Reaction Analysis (NRA) performed on these samples, after the supercritical fluid stripping treatment, was used to verify that the photoresist was effectively removed, while Scanning Electron Microscopy (SEM) showed that the treatment process has no detrimental effects on metallizations. These results indicate that the new treatment method is fully compatible with existing IC fabrication processes. Experimental results of the supercritical fluid treatment system will be presented, and the design and implementation to existing IC fabrication facilities will be discussed.

1. INTRODUCTION

1.1. Supercritical fluids

The temperature at which the vapor pressure above a pure liquid reaches one atmosphere is known as the normal boiling point. For water, the normal boiling point at one atmosphere is 100°C. In an open container, Figure 1, the temperature of liquid water cannot be raised above 100°C since this would cause the vapor pressure of water to rise above one atmosphere, which would exceed the ambient pressure conditions. If we place a quantity of water in a sealed container, however, then we may heat the liquid water to higher temperatures, so that the vapor pressure of the water can reach quite high values. As we uniformly heat the sealed container, the density of the liquid water decreases through thermal expansion. Simultaneously, the density of the water vapor increases. We can continue this heating process until the density of the liquid has been so reduced, and the density of the vapor phase has been so increased, that the two densities become equal. The temperature where the liquid and vapor densities become equal is called the critical temperature. Since the temperature inside the sealed container is everywhere equal, and the density is everywhere equal, thermodynamics dictates that the pressure inside the container be everywhere equal. This pressure is called the critical pressure. A fluid (liquid or gas) which has been brought to conditions above its critical temperature and pressure is known as a supercritical fluid.
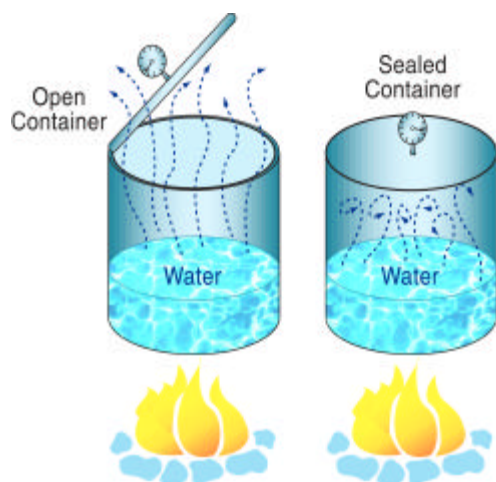
Figure 1. Schematic illustration of supercritical fluid formation by heating of a liquid in a sealed vessel.

Figure 2. Pressure-temperature-density surface for pure CO_2.

This physical description of the formation of a supercritical fluid suggests that all simple fluids can be made supercritical by generating the appropriate conditions of temperature and pressure. This is indeed correct, and Table 1 gives the critical temperatures and pressures of some common fluids.

Supercritical fluids are used as solvents in many commercial applications, including the extraction of caffeine from coffee, fats from foods, and essential oils and spices from plants. The attractiveness of supercritical fluids as solvents stems from their unique combination of liquid-like and gas-like properties. Table 2 gives a comparison of some physico-chemical properties of a typical organic fluid in the liquid, supercritical, and gaseous states. To a first approximation, the solvent power of a fluid is related to its density. The high, liquid-like densities achievable in supercritical fluids therefore allow for substantial solubilities. Figure 2 shows the

pressure-temperature-density surface for pure carbon dioxide. The critical point for pure CO_2 (31°C and 1072 psi) is shown in the figure by the large, solid circle. It can be seen that relatively small changes in temperature or pressure, near the critical point, result in large changes in density. It is this tunability of density, and therefore tunability of solvent power, which is the most attractive attributes of supercritical fluids. Also, the gas-like properties of low viscosity and high diffusivity of supercritical fluids provides for effective mass transport into granular, micro-porous, and polymer matrices. Finally, the absence of surface tension provides for excellent wettability.

In the supercritical state, $SCCO_2$ behaves as a classical, non-polar "organic" solvent, similar to hexane. Consequently, pure $SCCO_2$ is good for solubilizing other, non-polar materials, such as oils and greases. To solubilize polar substances, such as water, it is common to add "modifiers", which increase the polar nature of the fluid. Common modifiers are methanol and acetone.

Supercritical fluids based on CO_2 are an excellent choice for scale-up to industrial processes for several reasons. CO_2 is non-toxic, non-flammable, and inexpensive. Its critical conditions are easily achievable with existing process

Table 1. Critical temperature and pressure for some common fluids.

Fluid	Critical temperature (°C)	Critical Pressure (psi)
Neon, Ne	-229	400
Nitrogen, N_2	-147	492
Argon, Ar	-122	706
Xenon, Xe	17	858
carbon dioxide, CO_2	31	1072
Sulfur hexafluoride, SF_6	46	545
propane, C_3H_8	97	617
ammonia, NH_3	133	1654
water, H_2O	374	3209

Table 2. Comparison of physico-chemical properties of a typical organic fluid in the liquid, gas, and supercritical fluid state.

	Diffusivity (cm^2/s)	Viscosity (cP) or (mN·s/m^2)	Density (kg/m^3)
Liquid	10^{-5}	1	1000
Supercritical Fluid	10^{-3}	10^{-2}	300
Gas	10^{-1}	10^{-2}	1

equipment. Also, there is already an extensive transportation infrastructure, as virtually all restaurants serve carbonated drinks, which require the use of pressurized CO_2 cylinders. This unique combination of physical, chemical and economic properties of supercritical fluid CO_2 ($SCCO_2$) has prompted an evaluation into its use as a replacement for less-environmentally-friendly chemicals currently used for industrial manufacturing processes, including the semiconductor manufacturing processes for wafer cleaning, deposition, etching, photoresist stripping, and wastewater treatment.

In order to make the best use of a supercritical fluid as a solvent, it is desirable to use a flowing, closed-loop system. Figure 3 shows a schematic pressure-temperature phase diagram for CO_2, which also incorporates a process flow diagram for a closed-loop supercritical fluid treatment system. The treatment cycle begins with a liquid-CO_2 storage reservoir. The liquid is brought to above its critical pressure during a pumping operation, which sends the pressurized liquid to a heating unit. The heating unit warms the pressurized CO_2 to above its critical temperature, so that a supercritical fluid is formed. The supercritical fluid enters the treatment vessel and is brought into contact with the substrate. It is during this time that the materials to be removed are solubilized in the CO_2. There is a constant flow of CO_2 through the treatment vessel, so that clean, dry CO_2 is continuously made available. On exiting the treatment vessel, the $SCCO_2$, containing the dissolved material, is sent to a separation vessel. In the separator, the $SCCO_2$ is de-pressurized to a gas, reducing the CO_2 density to a gas-like value. The solubility of the entrained materials in the low-

Figure 3. Pressure-temperature phase diagram of pure CO_2 with a superimposed flow diagram for a closed-loop supercritical fluid treatment process.

density CO_2 gas is greatly reduced and are deposited in the bottom of the separator. The clean CO_2 gas exits the top of the separator, where it is chilled to liquefaction by a cooling unit before re-entering the storage vessel.

Such a closed-loop system means that there are no waste streams exiting the system. All of the extracted materials are retained in the separation vessel for subsequent analysis, recycle, treatment and/or disposal. Further, the extracted/removed materials are concentrated in the separator, greatly reducing the volume of waste.

1.2. Supercritical CO_2 as a surface-cleaning solvent

The Montreal Protocol and its subsequent modifications mandate a phase-out of the manufacture and use of CFC's. This has prompted an intensive search for alternative cleaning solvents. HFC's, seen as potential replacements, can generate corrosive compounds if subjected to high temperatures, and it is not clear that these compounds satisfy toxicity issues. Further, it is likely that these compounds, too, will eventaully be subjected to regulatory limitations. Aqueous-based systems have received wide attention, but these systems generate large waste streams, and the inherently high surface tension of these solutions limits their use in cleaning substrates containing very-fine-scale structures. Surfactants can be used to reduce surface tension, but this necessitates a subsequent rinsing and drying step, requiring large amounts of DI water

$SCCO_2$ is excellent for solubilizing lower molecular-weight organics, such as greases, oils, lubricants and fingerprints. In addition, the low surface tension and low viscosity of $SCCO_2$ promote particulate removal by significantly reducing the thickness of the surface boundary flow layer. Table 3 illustrates the desirable physical and chemical properties of dense-phase (supercritical and liquid) CO_2 compared to some commonly used liquid cleaning solvents. There has been considerable work done in developing supercritical fluids, and $SCCO_2$ in particular, for the precision-cleaning of inorganic surfaces,[1,2,3] including metals,[4,5,6,7] optical elements,[8] Si wafers,[9] and micro-electromechanical devices fabricated on Si.[10,11,12]

The advantage of $SCCO_2$ cleaning is that the process leaves no residues, since it evaporates completely when depressurized. As a result, subsequent rinsing and drying steps are not required. There is a commercial system available for micro-electromechanical device fabrication, and large capacity systems for machine part fabrication are being planned.
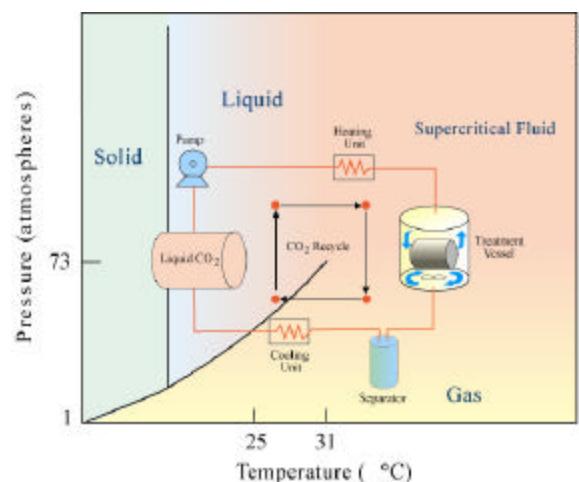
Table 3. Physico-chemical properties of dense-phase carbon dioxide and some common cleaning fluids. (Typical values at ambient conditions unless otherwise stated.)

Solvent	Viscosity (cP) or (mN·s/m^2)	Surface tension (dynes/cm) or (mN/m)	Relative dielectric constant	Dipole moment (Debye)	Density (kg/m^3)
Liquid CO_2	0.08 (@ 20°C, 105 atm)	1.5 (@ 20°C, on the boiling line)	1.6 (@ 0°C, 100 atm)	0	870 (@ 20°C, 105 atm)
Supercritical fluid CO_2	0.03 (@ 35°C, 75 atm)	≡ 0 (above the critical point)	1.3 (@ 35°C, 80 atm)	0	300 (@ 35°C, 75 atm)
1,1,1-tricholorethane	0.81	25.2	7.5	1.7	1300
methanol	0.54	22.1	32.7	1.7	800
water	1.00	72.0	78.5	1.8	1000

1.3. Supercritical CO_2 as a media for thin film deposition

SCCO$_2$ has been used as a deposition media for the production of metallic powders and thin films.[13,14] A chemical pre-cursor, such as an organo-metallic compound, is dissolved in the supercritical fluid, which is then expanded through an orifice, producing a fine aerosol of the dissolved precursor. In the neighborhood of the substrate, the finely-divided precursor is made to deposit the metal by a thermal decomposition, hydrolysis, oxidation or reduction reaction.[15,16,17]

There are several advantages in using a supercritical fluid-based deposition technique, compared to conventional methods. First, *any* metal-bearing compound that can be made soluble in SCCO$_2$ can be used as a pre-cursor material. CVD, on the other hand, requires the use of highly-volatile source materials. Also, a *single* supercritical fluid can be made to simultaneously deposit a multicomponent film, whereas CVD usually requires the use of multiple sources, with the attendant control systems for flow, temperature, *etc*. Supercritical fluid deposition, like CVD, can produce conformal depositions over complex shapes, in contrast to line-of-sight methods, such as electron-beam and thermal evaporation and sputter deposition.

In addition to metals, other materials of interest to the microelectronics industry have been synthesized in supercritical fluids, including SiO$_2$ films in supercritical alcohol,[18] nitrides and sulfides in supercritical ammonia,[19,20,21] sulfides in supercritical amines,[22,23] transition metal oxides in supercritical water,[24] in SCCO$_2$,[25] and in supercritical alcohol,[26,27] and rare-earth-based phosphors in SCCO$_2$.[28].

1.4. Supercritical CO_2 as a media for metal etching

Conventional etching processes, such as RIE, use directed beams of highly reactive species. These reactive species interact with the material to be etched, producing a volatile compound. This volatile compound is then swept away by a carrier gas. An etching process using supercritical fluids would be phenomenologically similar, in that a uniform etching environment is created at all points on the substrate surface, with the volatilized material being swept out by the flowing (supercritical) carrier gas.

There does not appear to be as much research done in this area as in the previous two applications, but there is nothing which would preclude the use of a reactive component, dissolved in an appropriate supercritical fluid, to etch Si, SiO$_2$, or metals. The potential advantage of SCCO$_2$ etching is an enhanced etching rate resulting from the low viscosity and high diffusivity.

1.5. Supercritical CO_2 as a photoresist fixer/developer

It has been demonstrated that the lower molecular weight fractions remaining after the exposure of specially-formulated, positive-tone [29] and negative-tone [30,31,32] photoresists to UV radiation can be selectively solubilized in SCCO$_2$. This type of matched supercritical fluid/photoresist system offers considerable promise as an environmentally-friendly lithography process, owing to the greatly reduced waste volume which would be generated.

It has been shown that the baking, or thermal "fixing", step of x-ray photoresist processing can be replaced by SCCO$_2$ extraction.[33] Instead of driving off the volatile solvent by oven heating, SCCO$_2$ can selectively extract the volatile

components. The advantage, once again, is the greatly-reduced levels of airborne solvent vapors.

The performance of conventional photoresists, such as those based on Novolak resins, can be enhanced by pre-processing in supercritical fluids. It is well-known that the chemical and thermal properties of photoresists, such as dissolution rate and glass transition temperature, T_g, are sensitive functions of molecular weight. A typical photoresist polymer is made up of a large range of molecular weights, and the variability in this molecular weight distribution has been implicated in observed variations in lot-to-lot photoresist peformance. A photoresist, dissolved in a supercritical fluid can be fractionated, or separated into a number of discrete molecular weight fractions. Once the photoresist has been "sorted" by molecular weight, these fractions can be recombined, or re-blended, into a formulation having a more optimal combination of properties.[34] For example, the very low molecular weight fractions, having a very low T_g and very high dissolution rate, as well as the very high molecular weight fractions, having a very high T_g and very low dissolution rate, can be removed or added in lesser proportions, to give a photoresist with a better overall combination of properties.[35]

1.6. Supercritical CO_2 as a photoresist-stripping solvent

The use of dense (liquid/supercritical) CO_2 for the selective removal of components during the developing stage of photoresist patterning has been previously described. A more difficult problem is the complete removal of photoresist after "fixation" by hard-baking. This baking treatment renders the resist much more resistant to chemical and physical attack, which is required for subsequent component fabrication. Consequently, the stripping of these materials has not received the level of attention, or success, as have the other applications.[36] It is this application which has been the focus of our research, and will be described in the next section of this paper.

1.7. Supercritical fluids for waste treatment

The use of supercritical fluids, particularly supercritical water, for the destruction (complete oxidation to CO_2 and H_2O) of organic compounds has been an industrial process for some time.[37,38] A recent example of its application to semiconductor manufacturing wastewater is given by Tomioka *et al*,[39] who report the complete conversion of tetramethylammonium (TMA) hydroxide, used as a postive photoresist developer, into N_2 using a Pd catalyst in supercritical water.

The advantage of supercritical water oxidation is the possibility of complete destruction of the target materials, into an environmentally benign form, in a semi-continuous process.

2. EXPERIMENTAL

2.1. Supercritical CO_2 as a photoresist-stripping solvent

The stripping of hard-baked photoresists generates more waste than any other step in the IC manufacturing process. Unfortunately, alternative processing strategies, which can significantly reduce waste generation, and personnel exposure, have not been forthcoming. This is due, in part, to the severe requirements placed on the stripping process, in terms of residual contamination and materials compatability.

It has been found [40] that pure, liquid propylene carbonate, (1,3-Dioxolane-2-one, 4-methyl;   CAS # 108-32-7), hereafter refered to as PCO_3, is an effective, low-toxicity replacement for methylene chloride and methyl chloroform in the debonding of a negative, PMMA-based photoresist (RISTON T168). This finding, and the fact that PCO_3 is not expected to adversely affect thin-film metallizations, promted us to investigate the use of PCO_3, as a $SCCO_2$ modifier, for its ability to remove hard-baked photoresists currently used by the Hewlett-Packard Company.

PCO_3 is an environmentally-friendly solvent, having no Personal Exposure Limit (PEL). It is non-flammable, non-toxic, biodegradible, and has a low vapor pressure.[41,42] It is readily available in high purity and in large quantities. Finally, PCO_3 is completely miscible with high-pressure CO_2.[43]

We have performed experiments on metallized Si wafers coated with hard-baked, positive-acting photoresists, and unmetallized Si wafers with positive-acting photoresists after ion-implantation treatments.

2.1.1. Nuclear Reaction Analysis (NRA)

Nuclear Reaction Analysis (NRA) was used to evaluate the degree of removal of photoresist from the treated Si wafers. NRA is a rapid (< 15 min.) analytical method which probes a relatively large surface area ($\approx$ 10 mm^2). The method provides a high degree of sensitivity to carbon (the main component of photoresists), and is non-destructive both to the substrate and to the metallizations. As a result, we are able to obtain high-precision, quantitative data on residual carbon concentration at the sample surface,

while preserving the samples for subsequent electron microscopy analysis.

In an NRA experiment, Figure 4, a beam of 1.2 MeV deuterons is directed onto the wafer surface. Carbon nuclei have an absorption resonance for deuterons at this energy, so that the deuterons are "absorbed", temporarily raising the carbon nuclei to an excited-state. The carbon atoms relax by emitting a high-energy proton, which is detected. The overall nuclear reaction can be written :

$$d^+\left(1.2\text{MeV}\right) + {}^{12}\text{C} \rightarrow {}^{13}\text{C} + p^+\left(3.1\text{MeV}\right)$$
(1)
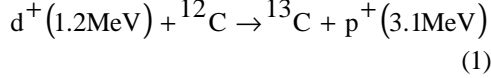
where d^+ is the incident deuteron and p^+ is the emitted proton. The sensitivity of NRA is high, owing to the fact that the emitted protons are of much higher energy than the incident deuterons, so that there is inherently a very large signal/noise ratio.

The fundamental equation relating areal density of surface carbon nuclei to resonance absorption cross-section of carbon nuclei is

$$nt\left(\frac{\text{atoms}}{\text{cm}^2}\right) = \frac{\left[Y\left(\text{yield}\right)\right]}{\left[\sigma\left(\frac{\text{cm}^2}{\text{str}}\right)\right]\left[Q\left(\text{atoms}\right)\right]\left[\Delta\Omega\left(\text{str}\right)\right]}$$
(2)

where σ is the resonance cross section, Y is the experimental yield (in detected number of protons for a given number of incident deuterons), (nt) is the areal density of surface carbon atoms, Q is the number of incident, singly-charged deuterons, and $\Delta\Omega$ is the solid angle of the proton detector. For the beam line and experimental procedure used in these analyses, $\Delta\Omega = 2.5 \times 10^{-3}$ str, $\sigma = 90 \times 10^{-27}$ cm^{-2}, $Q = 4$ μC. The areal density of carbon atoms, nt, is therefore related to the experimental yield (or number of detected protons), Y, by

$$\left[nt\left(\frac{\text{C atoms}}{\text{cm}^2}\right)\right] = 1.78 \times 10^{14} \cdot Y$$
(3)

To further enhance the experimental sensitivity for some of experimental runs, the sample is tilted, relative to the incident deuteron beam, to achieve a longer interaction, or 'path', length. For those experiiments, the samples were tilted at 60° relative to the incident beam, so that the right side of Eq. (3) must be multiplied by $\cos(60°) = \frac{1}{2}$. The experimental sensitivity, *in the absence of background*, is defined by an experimental yield of one count, Y = 1, so that we have

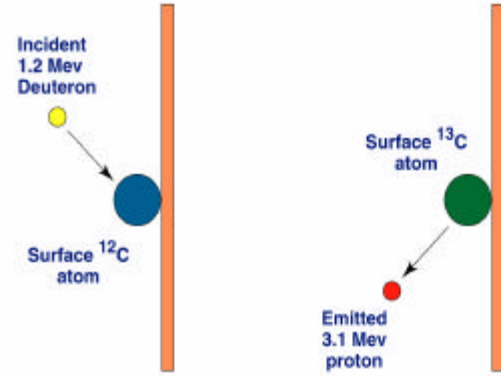## ^{12}C(d,p)^{13}C Nuclear Reaction Analysis

Figure 4. Schematic illustration of the Nuclear Reaction Analaysis (NRA) experiment.

$$\left(nt\right)_{60°,\text{min}} = 8.9 \times 10^{13}\left(\frac{\text{C atoms}}{\text{cm}^2}\right)$$
(4)

For comparison, an areal density of $1 \times 10^{15}\left(\frac{\text{atoms}}{\text{cm}^2}\right)$ is approximately equal to a monolayer of carbon atoms.

Column 2 in Table 4 gives the experimental yield (number of detected protons) for postive-tone resist-coated Si wafers containing Ti/Pt, In/Sn oxide, Al, and Ti/W metallizations, and two unmetallized, ion-implanted positive-tone resist coated wafers examined in this study. Column 3 gives the number of carbon atoms determined from the yield, while column 4 gives the equivalent number of monolayers of carbon remaining on the wafer surface, found by dividing the quantity (nt) by $1 \times 10^{15}\left(\frac{\text{C atoms}}{\text{cm}^2 \cdot \text{monolayer}}\right)$. It is seen that the residual carbon on the wafer surfaces, after the SCORR treatment, amounts to 1-10 atomic layers. This is not considered significant since the method used to correct the experimental gross yield for extrinsic carbon is only approximate, and will, if anything, be a low estimate. Further, the SCORR treatments were carried out in an open laboratory, and not in a clean-room environment and the NRA results will include carbon in the form of CO_2 left absorbed on the substrate surface during the final "rinse" step of the treatment as well as atmospheric CO_2 which is adsorbed during sample transfer between the treatment facility and the NRA facility.

2.1.2. Scanning Electron Microscopy (SEM)

Verification of photoresist removal represents only the first step of our research goal. The required second step is to demonstrate that the SCORR treatment is not destructive to pre-fabricated thin-film metallizations. We therefore performed SEM analyses on the 'stripped', metallized Si wafers to see if the metallizations are in any way undercut or etched. All microscopy was done on the same samples which were analyzed by NRA. No conductive coating was applied, so that low-voltage microscope operation was necessary. Further, all images were obtained with the sample tilted at 40° relative to the axis of the electron column to observe any undercutting of the metallizations.

Figure 5 shows a composite of four EM micrograph of the same Al/Si sample which was treated with the SCORR process and subsequently analyzed by NRA. No etching, pitting, or undercutting are evident. A similar absence of deleterious reactions was seen for the remaining metallized samples, indicating that the supercritical fluid composition and treatment parameters are compatible with existing IC processing procedures.

3. DISCUSSION

During the course of the SCORR experimental program, we have found that only by combining the the PCO_3/CO_2 mixture in a pulsed-flow system could complete photoresist removal be achieved. The mechanism by which the SCORR solvent removes the photoresist has not yet been determined. However, it is well known that polymeric materials can be made to swell by diffusion of CO_2 molecules and, in some instances, a significant reduction in the glass transition temperature can be produced. It is likely that such a swelling occurs, effectively softening the resist. Concomittantly, the reactive ester group of the PCO_3 acts to degrade the polymer, reducing its average molecular weight. Such a reduction promotes solubility in the supercritical fluid, promoting its removal.
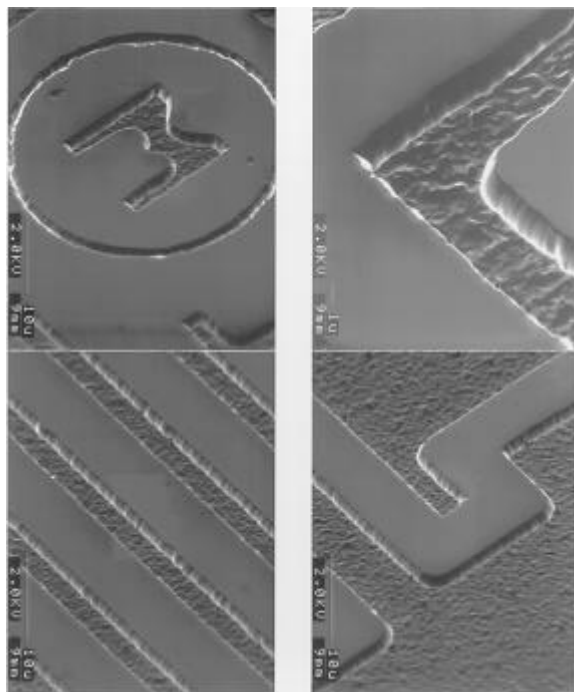

Figure 5. Composite of four electron micrographs of the SCORR-treated Si wafer with aluminum surface metallizations.

The actual treatment schedule for the samples we have examined thus far was arbitrarily chosen, and only limited experimentation has been devoted to process optimization. We have determined, however, that increasing the treatment temperature significantly increases the amount of photoresist softening, for a given treatment time, and would therefore be expected to significantly reduce the required, overall treatment time. Further, it must be established by electrical testing that there is no adverse effect of the SCORR treatment on pre-fabricated surface and sub-surface structures. Finally, additional work needs to be done on characterizing, using completed, production-size wafers, contamination due to widely-dispersed particulates and trace concentrations of transition metals.

Table 4. NRA results for the four Si/metallization systems treated by the SCORR process.

Sample description	Experimental gross yield, Y (counts)	(nt) $\left(\dfrac{\text{carbon atoms}}{\text{cm}^2}\right)$	Equivalent conc. of surface carbon atoms
Al on Si w/(+) resist	189 *	$(1.0 \pm 0.1) \times 10^{16}$	≈ 10 monolayers
In-Sn oxide on Si w/(+) resist	138 *	$(5.9 \pm 1.1) \times 10^{15}$	≈ 6 monolayers
Ti/W on Si w/(+) resist	97 *	$(2.4 \pm 0.4) \times 10^{15}$	≈ 2 monolayers
Pt/Ti on Si w/(+) resist	74 *	$(2.7 \pm 3.6) \times 10^{14}$	< 1 monolayer
Si w/(+) resist, implanted with 5×10^{14} cm^{-2} p$^+$ @50 kV	84	$(3.4 \pm 1.8) \times 10^{15}$	≈ 3 monolayers
Si w/(+) resist, implanted with 6.2×10^{15} cm^{-2} As$^+$ @ 40 kV	101	$(6.4 \pm 1.8) \times 10^{15}$	≈ 6 monolayers

* - sample tilted 60° relative to incident beam

4. CONCLUSIONS

Preliminary results indicate that CO_2-based supercritical fluids are attractive alternative solvents for photoresist stripping. Such fluids, as part of an appropriately-designed, closed-loop treatment system, have the potential to significantly reduce waste generation and water use.

Although our research has focused on the photoresist-stripping step of the fabrication process, there are other fabrication steps which may benefit from supercritical fluid processing, Figure 6. Clearly, the same system which is used for photoresist removal can be used for initial wafer cleaning, where highly-efficient removal of greases, oils, and particulates is required. Further, it has been established that supercritical fluids can be used to deposit metallic and insulating thin films, and so could be used for generate interconnect lines, barrier layers and low-dielectric constant films. It is also possible to use supercritical fluids, containing dissolved, reactive components, to etch metal and oxide films. Finally, supercritical water oxidation is a proven method for the complete oxidation of organic compounds, and so could be used for the treatment of wastewater.
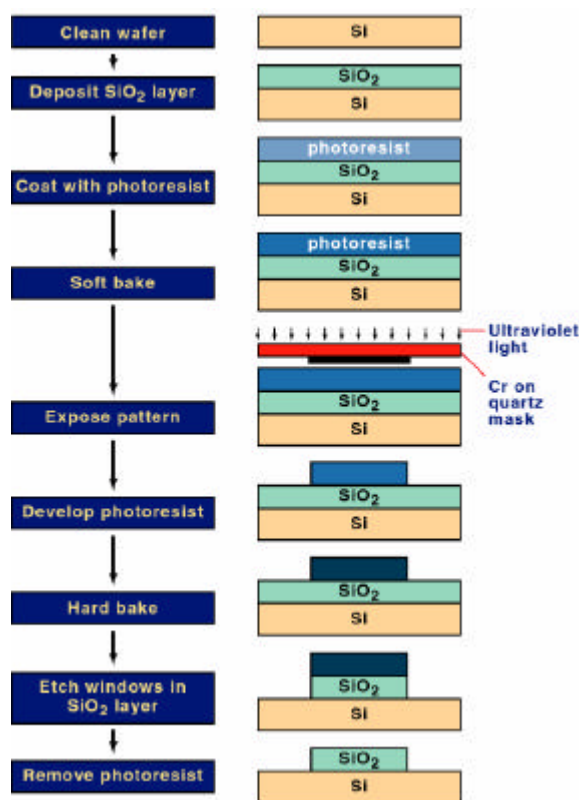

Figure 6. Schematic illustration of the photolithography process, illustrating some of the processing steps, which could be preformed using or replaced by supercritical fluids.

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